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(71) Applicant: MARINE SHALE PROCESSORS, INC. [US/US]; 110 James Drive West, Suite 120, St. Rose, LA 70087 (US).

(72) Inventors: BARTMAN, Candace, D. ; 124 Tom Drafts Circle, Gilbert, SC 29054 (US). RENFROE, James, H., Jr. ; 803 Spruce Street, Morgan City, LA 70380 (US). ROBARDS, Henry, L., Jr. ; 301 Richland Drive, Thibodaux, LA 70301 (US). CONNOLLY, Erin, M. ; Route 5, Box 862, Morgan City, LA 70380 (US).

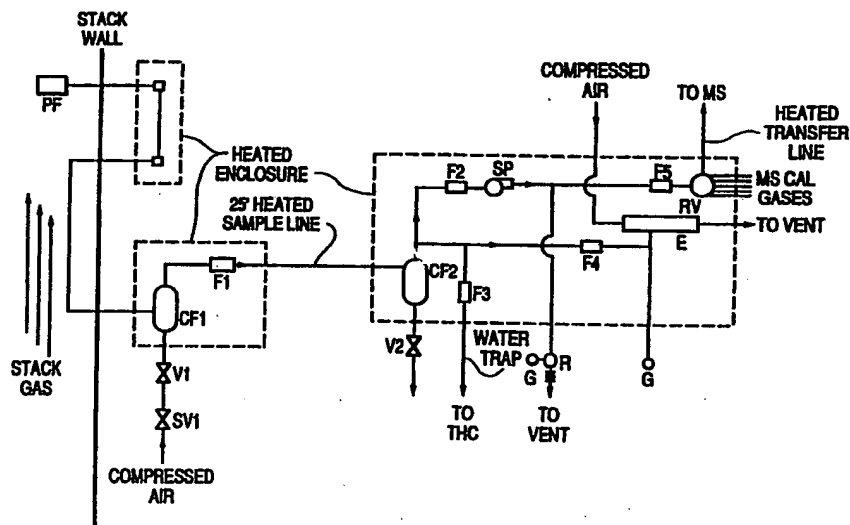
(74) Agents: TURNER, John, B. et al.; Finnegan, Henderson, Farabow, Garrett & Dunner, 1300 I Street, N.W., Washington, DC 20005-3315 (US).

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(54) Title: A MASS SPECTROMETER-BASED CONTINUOUS EMISSIONS MONITORING SYSTEM FOR HAZARDOUS WASTE STACK GAS MEASUREMENTS



(57) Abstract

A continuous emissions monitoring system for exhaust gas emissions containing HCl comprising a sampling subsystem with a sample probe in the effluent collecting effluent that is transmitted through heated conduits to filtering means and pump means to a mass spectrometer. The sampling subsystem is maintained at a temperature no less than about 190 °C and the flow rate through the system is greater than about 10 liters per minute. The process for continuous monitoring of exhaust emissions containing HCl extracts an exhaust gas sample and maintains the temperature and physical state of the exhaust gas through transport of the sample from the exhaust effluent to a mass spectrometer.

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Description

A MASS SPECTROMETER-BASED CONTINUOUS
EMISSIONS MONITORING SYSTEM FOR
HAZARDOUS WASTE STACK GAS MEASUREMENTS

Technical Field

Over the past several years, the need for limiting stack gas emissions at industrial facilities which process hazardous waste has become a topic of increasing importance. Government regulations are now pending for boilers and industrial furnaces burning hazardous waste as fuels or for recycling and methodology for continuous emissions monitoring systems (CEMS) is currently being evaluated.

Background Art

Among the compounds for which emissions limits will be set are HCl, SO₂, and nitrogen oxides, NO_x. At the present time, only a limited number of CEMS for HCl are installed in industrial environments and, as noted by Buonicore in "Experience with Air Pollution Control Equipment and Continuous Monitoring Instrumentation on Hazardous Waste Incinerators," *Journal of Hazardous Materials*, 1989, Vol. 22, pp. 233-242, the reliability of these systems has yet to be proven.

In December of 1989, the USEPA requested comments on "whether continuous emissions monitoring for HCl would be a feasible, practical requirement in lieu of waste analysis for chlorine to limit HCl emissions." The ASME Research Committee on Industrial and Municipal Wastes responded that only one of five monitoring devices found by the EPA to be "acceptable" was actually reliable in plant operations. The Committee noted that service and support on the device, which is based on infrared technology and produced in West Germany, has been inadequate to date. The Committee therefore concluded that continuous monitoring for HCl may be appropriate at large facilities but is inappropriate at smaller facilities.

A number of parameters in stack gas emissions can be used to evaluate the totality of the combustion process and the adequacy of the emission control system. For example the amounts of O_2 , CO_2 , SO_2 and nitrogen oxides, NO_x , present can indicate if the thermal degradation process is complete. See Oppelt "Incineration of Hazardous Waste, A Critical Review," *Journal of Air Pollution Control and Waste Management*, 1987, Vol. 37, No. 5, pp. 558-586, and C. Lee et al., "An Overview of Hazardous/Toxic Waste Incineration," *Journal of Air Pollution Control and Waste Management*, 1986, Vol. 36, No. 5, pp. 922-931, for reviews of the usefulness of these gases as indicators and the CEMS technology currently available for their measurement.

Products of incomplete combustion (PICs) are also components in stack gas for which public concern is high due to their potential toxicity. As noted by K. Lee in "Research Areas for Improved Incineration System Performance," *Journal of Air Pollution Control and Waste Management*, 1989, Vol. 38, No. 12, pp. 1542-1550, their formation and emissions of PICs are not well understood. Continuous monitors are not yet commercially available although Overton, "Development of Real-Time Stack-gas Analysis Methods," *Journal of Hazardous Materials*, 1989, Vol. 22, pp. 187-194, recently reported on a microbore gas chromatographic method which appears promising.

Continuous data for SO_2 and HCl emissions can help insure that these gases are adequately neutralized by the scrubbing system. As noted by Podlenski in "Feasibility Study for Adapting Present Combustion Source Continuous Monitoring Systems to Hazardous Waste Incinerators," *EPA Report No. 600/8-84-011a*, 1984, such data can provide information that can be used as a guide for design and operation purposes. At the present time, however, the EPA accepted technology for HCl monitoring is a manual sampling method with subsequent laboratory analysis by either titration or ion chromatography.

In order to improve performance at industrial facilities processing hazardous waste and to monitor stack

gas emissions for the purpose of risk assessment, there has been a longstanding need for a CEMS which efficiently monitors exhaust gases, especially HCl.

A CEMS consists of two major subsystems, an analytical subsystem and a sample extraction subsystem, each of which must be considered in the development of a complete system for continuous stack gas measurement. A variety of analytical technologies including gas chromatography, fourier transform infrared spectroscopy, photoacoustic spectroscopy, ion mobility spectrometry and mass spectrometry were evaluated and a commercially available mass spectrometer was chosen as the analytical subsystem. The advantages and disadvantages of the technologies mentioned above for this intended purpose has been discussed by Harlow et al., "Design of a Continuous Emissions Monitoring System at a Manufacturing Facility Recycling Hazardous Waste," *Proceedings, Hazardous Materials Control Research Institute, Great Lakes 90, Cleveland, OH*, pp. 285-289, 1990.

As noted previously, use of CEMS to monitor compounds such as O₂ and nitrogen oxides, NO_x is known. These compounds can be delivered to an analytical instrument while allowing the stack gas to cool since they are gases at routine ambient temperatures. In addition, none of these substances are very reactive, making sample extraction systems for these compounds relatively straightforward. There is no need for a heated system and most particulate material is removed with the water. However, conventional CEMS sample extraction is unsatisfactory for compounds such as HCl.

Disclosure of the Invention

The objective of this invention is to provide a mass spectrometer-based continuous emissions monitor with a heated sample extraction system. A further object of the present invention is to provide CEMS capable of continuous measurement of at least O₂, CO₂, SO₂, NO_x, and HCl. Another object of the present invention is to develop a heated sample extraction subsystem that would keep HCl in the

vapor phase, prevent corrosion and minimize problems associated with the reactive nature of HCl.

One embodiment of the present invention is a process for continuously monitoring the gaseous exhaust of an effluent stream containing HCl. The process comprises the steps of: extracting a sample of a gaseous effluent from an effluent stream; transporting the sample in a sample line within the effluent stream to maintain the sample at the desired sample temperature; hot filtering the sample; transferring the filtered sample through a heated transfer line to a heated analyzing station; maintaining a flow rate of the filtered sample of at least 10 liters per minute; and analyzing the filtered sample by mass spectrometry. Throughout the entire process the sample is maintained at a temperature no less than about 190°C.

Another embodiment of the present invention is a system for providing compositionally representative samples of the gaseous component of an effluent stream consisting of a mixture of gas, vapor and particulate material. The system comprises a sampling means within the effluent stream for continuously extracting samples of that stream; a conduit in flow communication with the sampling means, the conduit is heated by the effluent stream; a heated filtering system in flow communication with the conduit, the filtering system removes particulates from the samples; at least one heated transfer line in flow communication with the heated filtering system; an analyzer in flow communication with the transfer line, the analyzer comprises a heated sample pump and a heated capillary stem for sample introduction into a mass spectrometer, the pump is located in close proximity and upstream from the capillary stem and maintains a flow rate of at least 10 liters per minute within the sampling system. The sampling system, conduit, heated filtering system, heated transfer line and the sample pump are maintained at a temperature of not less than about 190° C.

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A third embodiment of this invention is a continuous emissions monitoring system comprising the heated sampling system described above and a mass spectrometer.

Brief Description of the Drawings

Figure 1 is a schematic drawing of the sample extraction subsystem according to a preferred embodiment of the invention.

Figure 2 shows the improvement in HCl response of the mass spectrometer after the above modifications.

Figure 3 is a detail drawing of (a) the probe connection in the sample extraction subsystem and (b) of a standard gas connection in the sample extraction system used for calibration.

Figure 4 is a plot of O₂ and HCl concentration versus time obtained while conducting the calibration error tests of Example 1.

Figure 5a shows the O₂ and HCl response curves when switching from blowback air to exhaust stack gas prior to modification for HCl analysis.

Figure 5b shows the O₂ and HCl response curves when switching from blowback air to exhaust stack gas after modification for HCl analysis.

Figure 6 is a plot of HCl gas concentration and percent error from the data obtained in the relative accuracy tests of the present invention in Example 2.

Best Mode for Carrying Out the Invention

The mass spectrometer-based continuous emissions monitoring system (CEMS) has two subsystems, the sample extraction subsystem and the mass spectrometer subsystem. The mass spectrometer subsystem, which measures the percent concentration of individual components of the stack gas sample, consists of the mass spectrometer hardware and the data acquisition equipment. The sample extraction subsystem's function is to deliver the stack gas sample to the mass spectrometer without changing the state or

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composition of the gaseous and vapor portions of the extracted sample.

Sample Extraction Subsystem

The design criteria for the sample extraction subsystem included:

- 1) heating of the system in its entirety to avoid water condensation with subsequent loss of HCl;
- 2) adequate filtration to remove particulate material larger than one micron;
- 3) a pumping system with sufficient capacity to draw the sample from the stack with minimum delay time; and
- 4) ease of maintenance.

Figure 1 shows a schematic of the preferred sample extraction system of this invention. A sampling means, preferably a sample probe consisting of a 30 micron filter mounted on a stainless steel tube, is installed inside the exhaust stack approximately 8 stack diameters downstream from the input conduits of the fans driving the effluent through the exhaust stack, and 8 stack diameters upstream from the effluent exhaust at the end of the stack. A sample line then runs through the exhaust stack and within the effluent to allow the heat of the exhaust stack to maintain the desired sample temperature, thus eliminating the need for a long transfer line that must be heated and maintained. The sample line may first run from the sampling means to a heated maintenance enclosure mounted on the exhaust stack wall which facilitates maintenance of the probe and provides a point for connection of standard gases used in calibration and testing.

At the base of the stack the exhaust sample line enters a second heated enclosure which houses a series of filters comprising a first filter, preferably a cyclone filter, to remove large particulates and a secondary filter, preferably a ceramic glass microfiber filter, to remove small particulates. Small particulates are those having sizes less than about 5 microns to about 0.1 micron. A source of compressed air may be connected to the first filter to

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blowback the system periodically to avoid sample line and filter blockage. The exhaust gas sample then passes through a heated transfer line to a heated analyzing station.

The heated analyzing station comprises a pump, preferably an eductor, is used to move at least 10 liters per minute, preferably about 15 liters per minute, of the exhaust gas sample from the stack to the enclosure upstream from mass spectrometer, and a heated capillary for sample introduction into the mass spectrometer. The analyzing station may also contain a second series of filters to further remove particulate material. Preferably the second series of filters comprises a cyclone filter to remove large particulates and a second ceramic filter to remove small particulates. Only particles smaller than 0.1 micron pass the final filter. After filtration, the exhaust gas sample may be split and directed to a total hydrocarbon analyzer. A second pump, preferably a diaphragm pump equipped with a backpressure regulator at the outlet side of the pump, insures that an appropriate flow of sample is delivered to the mass spectrometer. The filtered exhaust gas sample may be connected to the mass spectrometer via computer-controlled 16 position rotary valve which may also have connections to mass spectrometer calibration gases.

To accurately analyze for HCl it is critical to maintain the sample at the appropriate elevated temperature. The slightest cold spot that allows condensation of water not only removes HCl but causes particulate to drop out of the gas stream with subsequent blockage. For analysis of HCl, the system is heated to a temperature no less than about 190°C. In addition, HCl is an extremely reactive substance which can lead to corrosion. The elevated temperatures, which insure that HCl remains in the vapor phase, eliminates corrosion problems.

The reactive nature of HCl can lead to "wall affects", the adsorption to and desorption from surfaces. Construction materials are therefore an important consideration in minimizing these affects. Preferably materials such as

teflon and stainless material are used as they show the least propensity to adsorb HCl.

The following changes are preferably made to the mass spectrometer to reduce HCl adsorption and improve response. First, the rotary valve rotor and a mass spectrometer ferrule, ordinarily made of a graphite and vespel composite, are replaced with components made of teflon. Next, the mass spectrometer's ionizer, which has a large surface area, is replaced with an "open" ionizer constructed of wire mesh in an effort to reduce the surface area available in the mass spectrometer to adsorb/desorb HCl.

Figure 2 shows the improvement in HCl response of the mass spectrometer after the above modifications. The lower curve labelled "Initial" is the response prior to modification. The middle curve labelled "Teflon" shows the improvement with a change of material. The upper curve labelled "Open Ionizer" shows the improved response with the open screen-type ionizer.

Sample flow rate also appears to have a dramatic effect on the adsorption of HCl. It had been reported by Nelson that HCl has a tendency to adsorb on material surfaces at flow rates less than 10 liters per minute. See Nelson, "Continuous Measurement of HCl Emissions from MSW Incineration Facilities," *Proceedings, Air Pollution Control Association International Speciality Conference on the Thermal Treatment of Municipal, Industrial and Hospital Waste*, Pittsburgh, PA., p. 183 (1987).

Although the flow from the sample source in the exhaust stack to the outlet of the diaphragm pump was 15 liters per minute, the flow dropped dramatically at the rotary valve. Therefore, the fused silica capillary inlet of the mass spectrometer was moved from the common outlet of the rotary valve to the outlet of the diaphragm pump where flow rates are high. In the present invention flow rates greater than about 10 liters per minute, preferably about 15 liters per minute, which show a lower tendency for adsorption, are employed.

Relative accuracy tests for HCl were repeated with the modified instrument and inlet configuration. The data in Table 6 show that the relative accuracy for HCl obtained with the new configuration was 5.8%, well within the EPA requirement and more in line with the accuracies obtained for the other gases tested.

Mass Spectrometer Subsystem

The mass spectrometer used in the invention is a process mass spectrometer which continuously introduces the gas stream directly into the analyzer and monitors specific ion intensities for each component in the stream. A preferable mass spectrometer is a Questor Process Analyzer manufactured by Extel Corporation of Pittsburgh, Pennsylvania.

When the sample enters the mass spectrometer's vacuum chamber, it flows through a region referred to as an electron impact ion volume. Some percentage of the sample molecules collide with electrons thereby producing positively charged molecular ions and fragment ions. The ions thus formed are electrically removed from the ion region using a series of lenses and are "shot" into the quadrupole mass filter which separates the ions according to their mass-to-charge ratio. A mass spectrum, a plot of ion intensity versus mass-to-charge ratio, for every component is unique. In process mass spectrometry, a single ion is chosen for each component to be analyzed. In situations where the ion intensity is the result of several components in the stream, the component of interest is resolved mathematically by subtraction of the interfering components' ion intensities.

The components to be monitored are easily selected using the mass spectrometer's data system to create an "analysis method". In the present invention, the instrument is preferably set to continuously monitor SO₂, nitrogen oxides (as NO), HCl, Cl₂, N₂, O₂, CO₂ and Ar. An analysis of the eight components is completed every three seconds with the data reported locally and sent to the plant control computer. The instrument automatically calibrates

itself using certified standard blends which are connected to the rotary valve. The calibration routine takes approximately ten minutes to complete.

Reliability

Maintenance on the CEMS of the present invention is minimal. The mass spectrometer requires only routine cleaning and maintenance. The sample extraction system shows no signs of corrosion during the period in which it was developed and tested and requires minimal maintenance consisting of daily blowback and periodic changes of the system filters. Filter changes are required two to three times monthly and take approximately one hour.

The following examples are intended to illustrate, not limit, the present invention.

EXAMPLES

These examples compare and contrast the present invention with and without the modifications described above for HCl analysis. Example 1 was conducted without those modifications. Example 2 presents results obtained with the modified system.

The calibration drift, calibration error and relative accuracy (RA) test methods used in these examples are outlined by the Environmental Protection Agency in 40 CFR (Part 60, Appendix B, Specifications 3 and 4) and an EPA draft performance specification for HCl. These methods are summarized briefly below.

Sample Introduction

Standard gases are introduced in two ways. First, for direct mass spectrometer introduction, cylinders were connected to the rotary valve (see Figure 1) to introduce gas directly to the mass spectrometer. Introduction at this point bypasses all portions of the extraction system used for sample acquisition and conditioning and demonstrates the mass spectrometer's capabilities. Second, for introduction through the sample extraction system, standard gas cylinders are introduced at the maintenance enclosure for the probe. Figure 3a shows the normal probe connection at the stack.

For the tests conducted to assess sample system performance, the probe filter was disconnected and a tee inserted in its place (Figure 3b). A standard gas cylinder was connected to one side of the tee and the cylinder pressure adjusted until there was gas flowing out of the tee at atmospheric pressure. This insured adequate sample for the sample extraction system without pressurizing the system.

Calibration Drift Test

The calibration drift test measures the stability of the CEMS calibration over time. The test is performed on both zero and high level standards. After instrument calibration, standards are introduced through the sample extraction system and a zero time measurement taken. After 24 hours, during which no maintenance, repair or adjustment took place, the standards are again introduced and a second measurement taken, the 24-hour reading. After the 24-hour measurement, the instrument is calibrated and the next 0-time measurement taken. The test is generally repeated for seven consecutive days.

For each 24-hour period, the calibration drift is calculated by the equation:

$$\text{Calibration drift} = \frac{d}{\text{span value}} \times 100$$

where $d = (\text{0-time measurement}) - (\text{24-hour measurement})$

span value = the upper limit of the CEMS measurement range specified for the facility.

Calibration Error Test

The calibration error test is designed to assess the accuracy and linearity of the CEMS over the entire measurement range. After instrument calibration on a concentration equal to the span value, zero, mid and high level standards are each introduced three times through the sample extraction system.

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The calibration error is calculated by the equation:

$$\text{Calibration error} = \left| \frac{\bar{d}}{\text{span value}} \right| \times 100$$

where \bar{d} = mean difference between the CEMS response and the known reference concentration.

Relative Accuracy

The relative accuracy test is used to validate the calibration technique and verify the ability of the CEMS to provide representative and accurate measurements. The CEMS measurement is compared to a reference measurement obtained using an EPA accepted Performance Test Method (PTM). A minimum of nine tests is generally performed for each compound evaluated.

The relative accuracy is calculated by the equation:

$$\text{Relative Accuracy} = \frac{|\bar{d}| + |CC|}{\overline{\text{PTM}}} \times 100$$

where $|\bar{d}|$ = absolute value of the mean of the differences of the CEMS and PTM measurements

$|CC|$ = absolute value of the confidence coefficient
 $= t_{0.975} \frac{S_d}{\sqrt{n}}$

$\overline{\text{PTM}}$ = average reference measurement

EXAMPLE 1

In this example, only O_2 , CO_2 , and SO_2 were evaluated using a CEMS without the system modifications needed to ensure accurate HCl measurement as described above. As shown by the results below the system configuration used for these experiments was not adequate for accurately measuring HCl.

CEMS Configuration

Only O_2 , CO_2 , and SO_2 were evaluated since certified HCl standards were not available due to long delivery times from the gas manufacturer. Table 1 shows the comparison of

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the standard deviations (repeatability) obtained by introducing standards directly to the mass spectrometer and through the sample extraction system. The data compare well showing that the sample extraction system causes no degradation of the mass spectrometer response.

Table 1

Repeatability

	% Conc.	Direct Introduction Std. Dev.	% RSD	Through Sample Std. Dev.	System % RSD
O ₂	8.438	0.009	0.11	0.012	0.15
CO ₂	5.259	0.009	0.16	0.008	0.15
SO ₂	0.102	0.002	0.26	0.001	0.23

$$\% \text{ RSD} = \frac{\text{Std. Dev.}}{\% \text{ Conc.}} \times 100$$

% Conc.

A calibration drift test was performed to measure the stability of the CEMS calibration over time. The results in Table 2 show that the average calibration drift for O₂, CO₂, and SO₂ for the seven measurements was at least a factor of ten better than the EPA requirement.

TABLE 2

Calibration Drift Tests

Compound	% Conc. Tested	Average MS Drift	EPA Requirement
O ₂	0.00	0.02	0.5% from reference
O ₂	18.11	0.04	0.5% from reference
CO ₂	0.00	0.00	0.5% from reference
CO ₂	11.21	0.05	0.5% from reference
SO ₂	0.00	0.02	2.5% of span
SO ₂	0.248	0.04	2.5% of span

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A calibration error test was conducted for O₂, CO₂, and SO₂ and HCl to assess the accuracy and linearity of the CEMS over the entire measurement range. The results in Table 3 show that the calibration errors for all components meet the EPA specification when calculated using the EPA formula. However, the calibration error for HCl is significantly higher than the errors for O₂, CO₂, and SO₂.

TABLE 3

Calibration Error Tests

Compound	% Conc. Tested	MS Error %Span	EPA Requirement
O ₂	0.00	0.03	Not required
O ₂	8.40	0.11	Not required
O ₂	18.11	0.08	Not required
CO ₂	0.00	0.03	Not required
CO ₂	5.35	0.76	Not required
CO ₂	11.21	0.13	Not required
SO ₂	0.00	0.22	Not required
SO ₂	0.103	0.00	Not required
SO ₂	0.248	0.44	Not required
HCl	0.00	3.3	5.0% of span
HCl	0.0596	2.1	5.0% of span
HCl	0.1560	2.1	5.0% of span

Table 4a shows the mass spectrometer response for direct introduction of the mid level standards for HCl and O₂. In both cases, the errors are quite small, although it was noted that HCl took considerably more time to equilibrate to the certified value than O₂.

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Table 4a
Calibration Error
Standards Introduced Directly to the MS

Component	Certified Value	Measured Value	d	% Error
O ₂ (% Conc.)	8.40	8.44	0.04	0.48
HCL	596	593	3	0.50

Table 4b gives the data obtained during the calibration error test when standards were introduced through the sample extraction system.

Table 4b
Calibration Error
Standards Introduced through the Sample Extraction System

Component	Certified Value	Measured Value	d	% Error	Change Made
O ₂ (% Conc.)	8.40	8.42	0.02	0.24	Zero-Mid
O ₂	8.40	8.44	0.04	0.48	High-Mid
O ₂	8.40	8.42	0.02	0.24	Zero-Mid
HCL (ppm)	596	475	121	20.3	Zero-Mid
HCL	596	679	83	13.9	High-Mid
HCL	596	509	87	14.6	Zero-Mid

The O₂ data compare well to that obtained with direct introduction. The HCL data is very poor by comparison and appears to be dependent upon the last gas analyzed. For example, when changing from the zero gas to the mid standard, the measured reading was low whereas the measured reading was high when changing from the high to mid standard.

A plot of O₂ and HCL concentration versus time obtained while conducting the calibration error tests is shown in Figure 4 and further confirmed the system's sluggish response to HCL. The plot shows the mass spectrometer response when introducing the mid level and high level standards. Each data point is a one minute average of the

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mass spectrometer response. O₂ responded to the change in the gas standard within one minute and equilibrated to the certified concentration in less than three minutes whereas HCl had not equilibrated to the certified value after flowing the standard for 15 minutes.

Relative accuracy tests, designed to verify the ability of the CEMS to provide representative and accurate measurements, were conducted to further assess the CEMS' capability to analyze the gases of interest. The results in Table 5 show that O₂, CO₂, and SO₂ were well within the limits set by the EPA.

Table 5
Relative Accuracy Tests
Original CEMS Configuration

Compound	MS %RA	EPA Requirement
O ₂	3.8	20.0
CO ₂	2.5	20.0
SO ₂	5.8	20.0
HCL	22.1	20.0

EXAMPLE 2

The following tests were performed with the modifications for HCl analysis described above.

Figure 5a shows the O₂ and HCl response curves when switching from blowback air to stack gas. The O₂ and HCl delay times were 36 and 45 seconds, respectively. O₂ equilibrated within approximately 75 seconds but HCl had not equilibrated by 93 seconds. Figure 5b shows that with the modifications to the position of the fused silica capillary inlet described above the delay time for both O₂ and HCl was 27 seconds and that O₂ and HCl reached equilibrium within 39 and 54 seconds, respectively.

Relative accuracy tests for HCl were repeated with the modified instrument and inlet configuration. The data in Table 6 show that the relative accuracy for HCl obtained with the new configuration was 5.8%, well within the EPA

requirement and more in line with the accuracies obtained for the other gases tested. There is, however, a wide variation in % error with two samples having an error as low as 0.4% to the highest error of 10.9%.

TABLE 6

HCl Relative Accuracy

Run #	PTM (ppm)	MS (ppm)	d (ppm)	% Error
1	546	525	21	3.8
2	650	712	-62	9.5
3	721	800	-79	10.9
4	731	671	60	8.2
5	845	821	24	2.8
6	921	1009	4	0.4
7	1101	1097	4	0.4
8	1377	1382	-5	0.4
9	1385	1327	58	4.2

% RA = 5.8%

If the slower response time for HCl were related to higher % errors in the relative accuracy data, one would expect a high % error to occur when the concentration of HCl was rapidly changing during the sampling period and a low % error to be obtained when HCl concentration was relatively stable. Figure 6 is a plot of HCl concentration during the periods of each relative accuracy test with a bar to indicate the % error obtained for that sample. There appears to be little correlation between the % error and concentration stability. Runs #7 and 8 had the lowest % error but were taken during a period when HCl concentration changed dramatically whereas Run #4, for example, shows a much more stable level of HCl but a much higher % error. During these relative accuracy tests, there was a significant problem with leaks at the ground glass joints of the impingers used to

collect the stack gas for the performance test measurement which may have given rise to the variable % errors.

The results obtained in Examples 1 and 2 for the relative accuracy tests for O₂, CO₂, and SO₂ and HCl were well within the limits required by the EPA, indicating that a mass spectrometer with a carefully designed and implemented sample extraction appears to be a viable alternative for continuous monitoring of stack gas emissions.

The present invention has been disclosed in terms of a preferred embodiment, however, the scope of the invention is not limited to this embodiment. The scope of the invention is determined solely by the appended claims and their equivalents.

Claims

1. A process for continuously monitoring the gaseous exhaust of an effluent stream containing HCl, said process comprising,
 - extracting a sample of said exhaust from said effluent stream;
 - transporting said sample in a sample line within said effluent stream to heat said sample to the desired sample temperature;
 - hot filtering said sample;
 - transferring said sample through a heated transfer line to a heated analyzing station;
 - maintaining a flow rate of said sample of at least 10 liters per minute; and
 - analyzing said sample by mass spectrometry; wherein said sample is maintained at a temperature no less than about 190°C.
2. The process of claim 1 wherein said hot filtering step comprises filtration through a series of filters comprising a first filter to remove large particulates and a second filter to remove small particulates.
3. The process of claim 2 further comprising a second filtration step after said transferring step wherein said sample is passed through a second series of filters located within said analyzing station and which comprises a first filter to remove large particulates and a second filter to remove small particulates.
4. The processes of claim 3 further comprising a step, prior to said analyzing step, of splitting said sample into two portions and directing the first portion to a mass spectrometer and directing the second portion to a total hydrocarbon analyzer.
5. The process of claim 4 wherein the analyzing step continuously monitors SO₂, NO, HCl, Cl₂, N₂, O₂, CO₂ and Ar.

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6. The process of claim 1 wherein the analyzing step continuously monitors SO₂, NO, HCl, Cl₂, N₂, O₂, CO₂ and Ar.

7. A system for providing compositionally representative samples of the gaseous component of an effluent stream consisting of a mixture of gas, vapor and particulate material, said system comprising:

sampling means within said effluent stream for continuously extracting samples of said stream;

conduit means in flow communication with said sampling means, said conduit means being heated by said effluent stream;

heated filtering means in flow communication with said conduit means, said filtering means disposed to remove particulates from said samples;

at least one heated transfer line in flow communication with said heated filtering means;

analyzing means in flow communication with said transfer line, said analyzing means comprised of a heated sample pump and a heated capillary for sample introduction into a mass spectrometer, said pump being located in close proximity to and upstream from said capillary, said pump maintaining a flow rate of at least 10 liters per minute within said system,

wherein said sampling means, conduit means, heated filtering means, heated transfer line and said pump are maintained at a temperature of not less than about 190° C.

8. The system of claim 7 wherein said pump maintains a flow rate of at least about 15 liters per minute.

9. The system of claim 7 wherein said sampling means is comprised of a 30 micron filter mounted on a metal conduit.

10. The system of claim 7 wherein said effluent is conducted through a stack by means of at least one fan, said fan inputting effluent into said stack at a fan inlet, said

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sampling means being located approximately 8 stack diam ters downstream from said fan inlet.

11. The system of claim 7 wherein said effluent is conducted through a stack by means of at least one fan, said stack having an exhaust end, said sampling means being located approximately 8 stack diameters upstream from the exhaust end of said stack.

12. The system of claim 7 wherein said system includes a heated enclosure between said sampling means and said heated filtering means, said enclosure including means for providing maintenance to said sampling means.

13. The system of claim 12 wherein said heated enclosure between said sampling means and said heated filtering means includes means for injecting gas into said system in a direction opposite to flow of samples through said system.

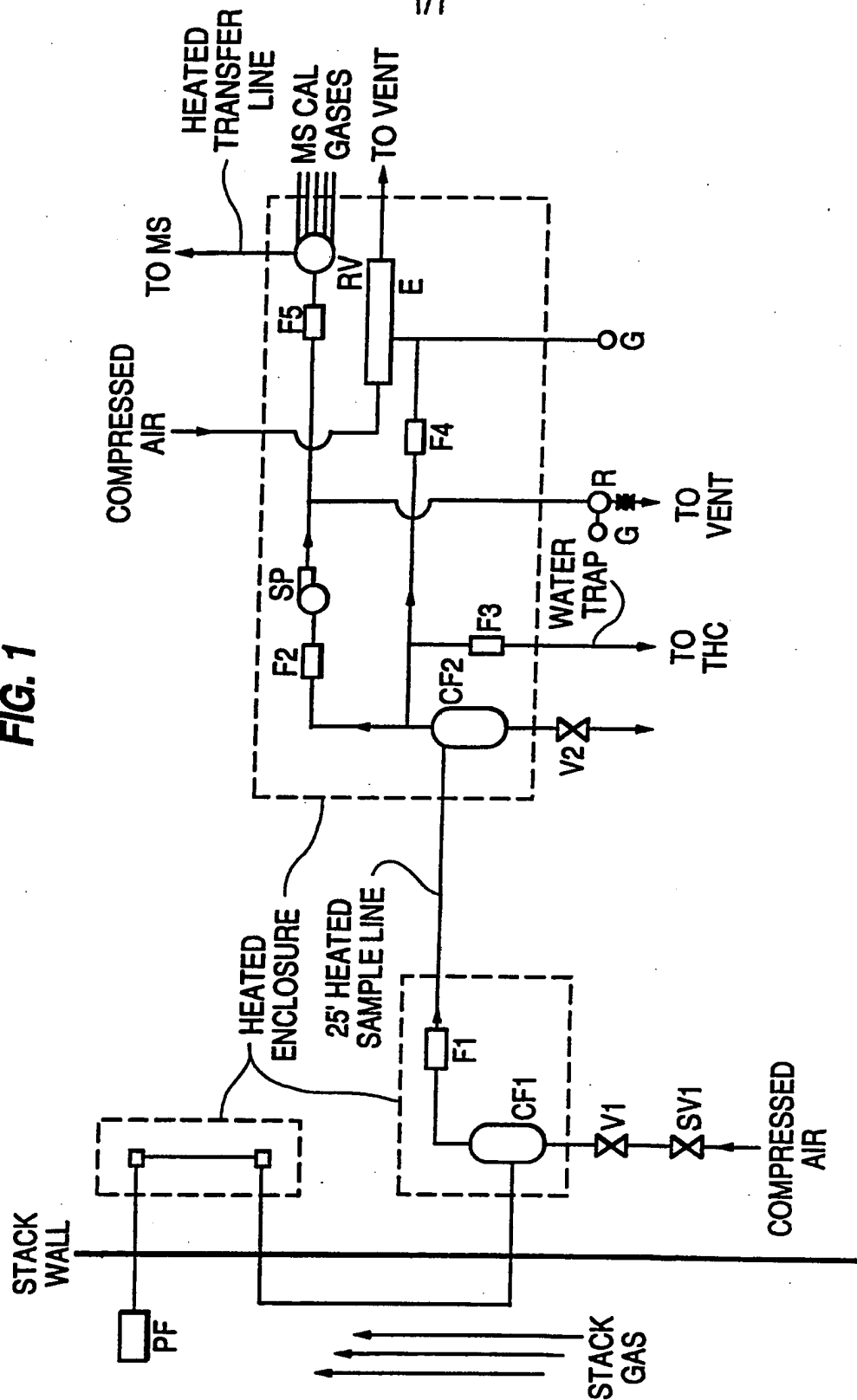
14. The system of claim 7 wherein said system includes a heated enclosure between said sampling means and said heated filtering means, said enclosure including means for injecting calibration gases into said system proximate said sampling means.

15. A continuous emissions monitoring system comprising the system of claim 7 and a mass spectrometer which includes a mesh type ionizing screen.

16. The system of claim 7 wherein said system includes a computer controlled multiport valve in flow communication with said mass spectrometer, wherein said multiport valve is constructed of stainless steel and teflon.

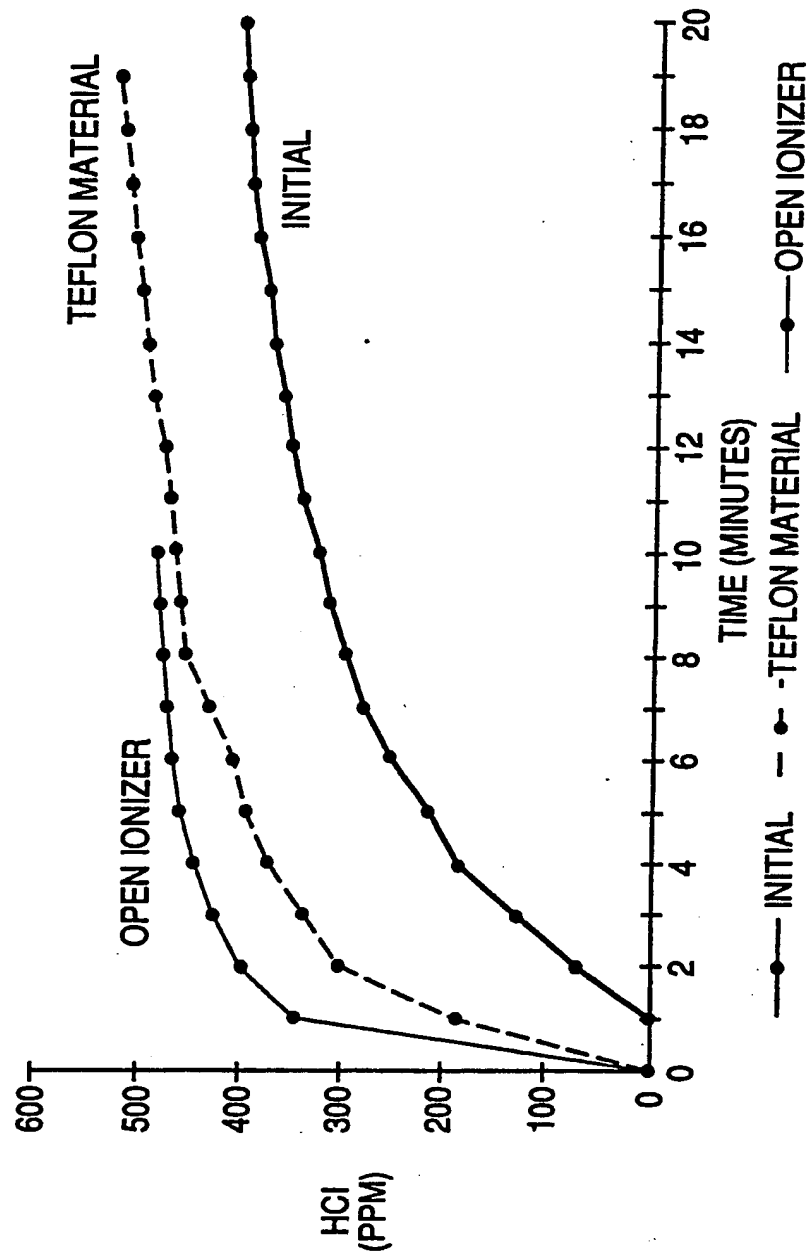
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FIG. 1



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FIG. 2



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FIG. 3b

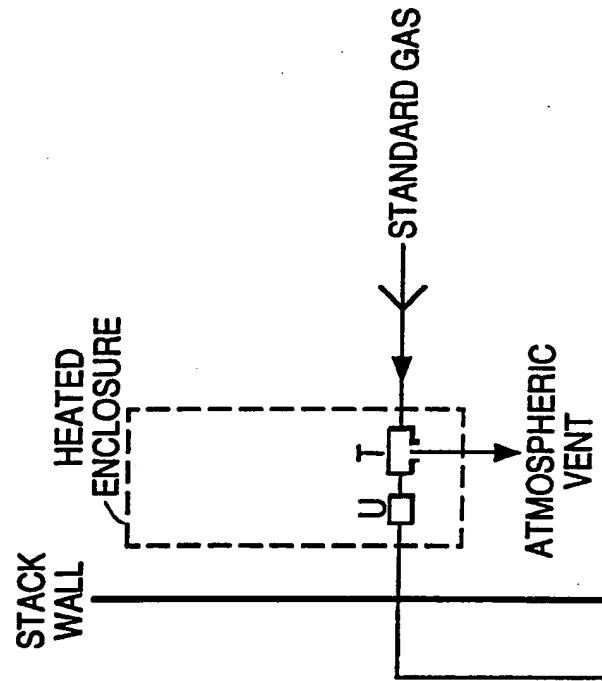
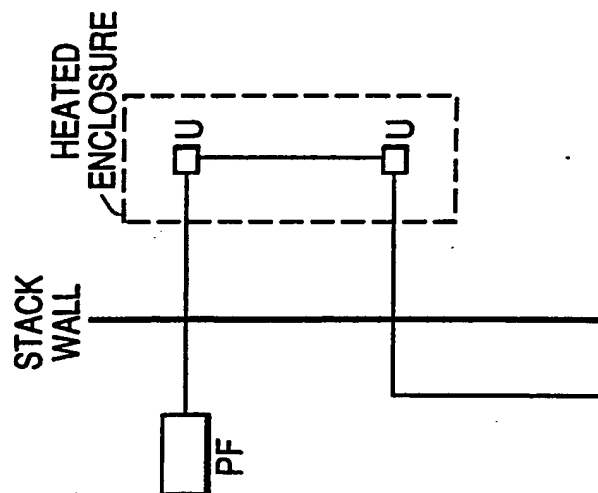
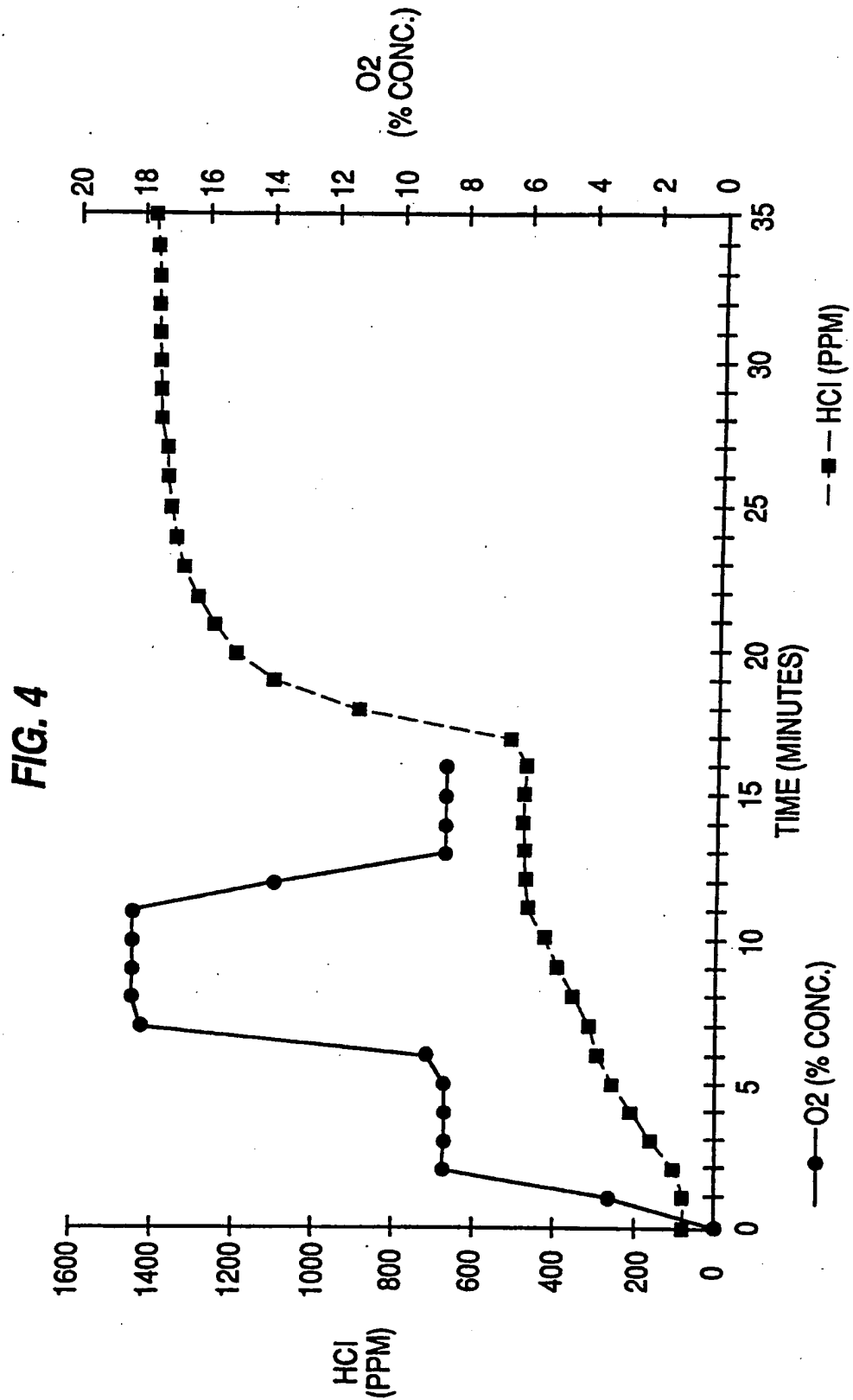


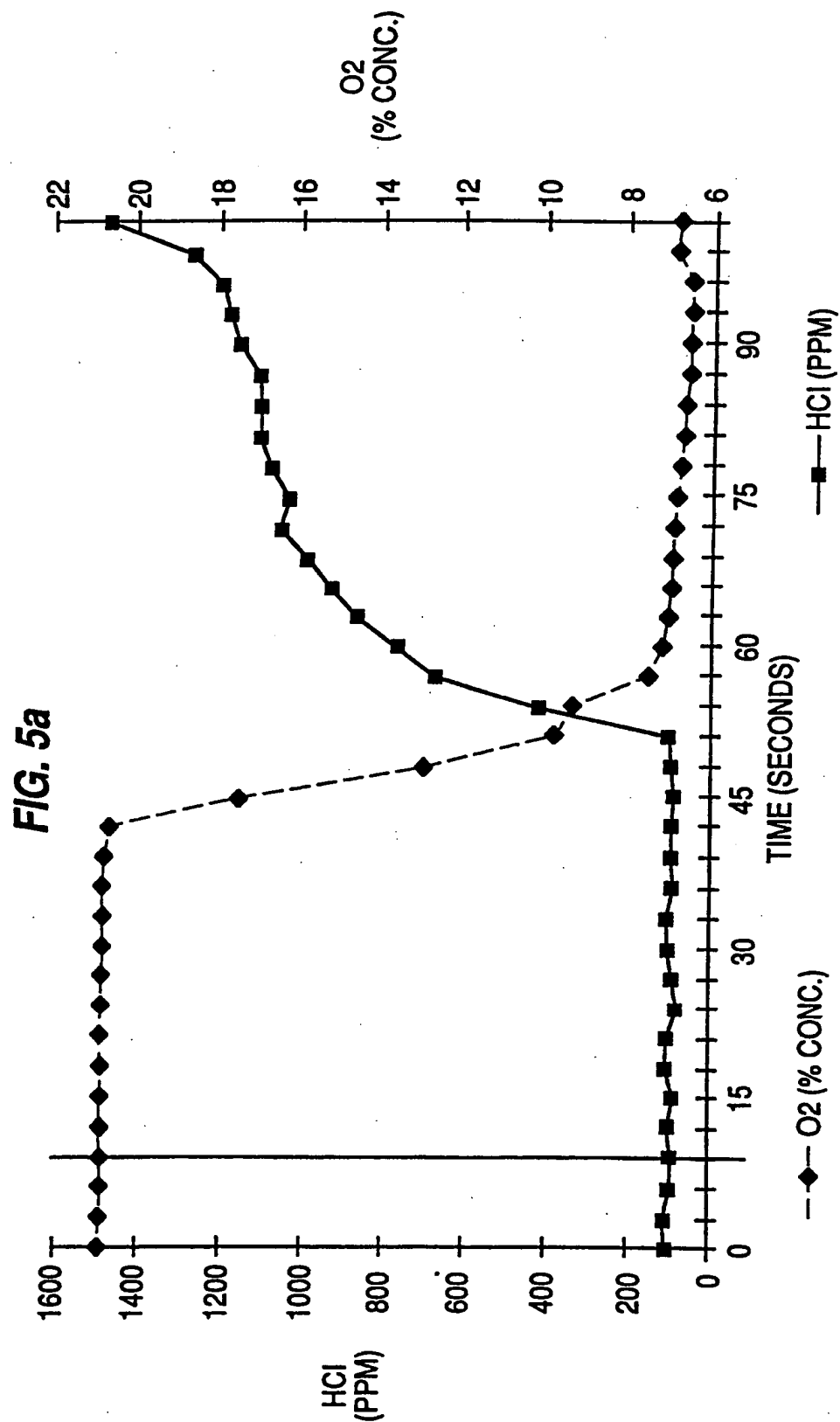
FIG. 3a



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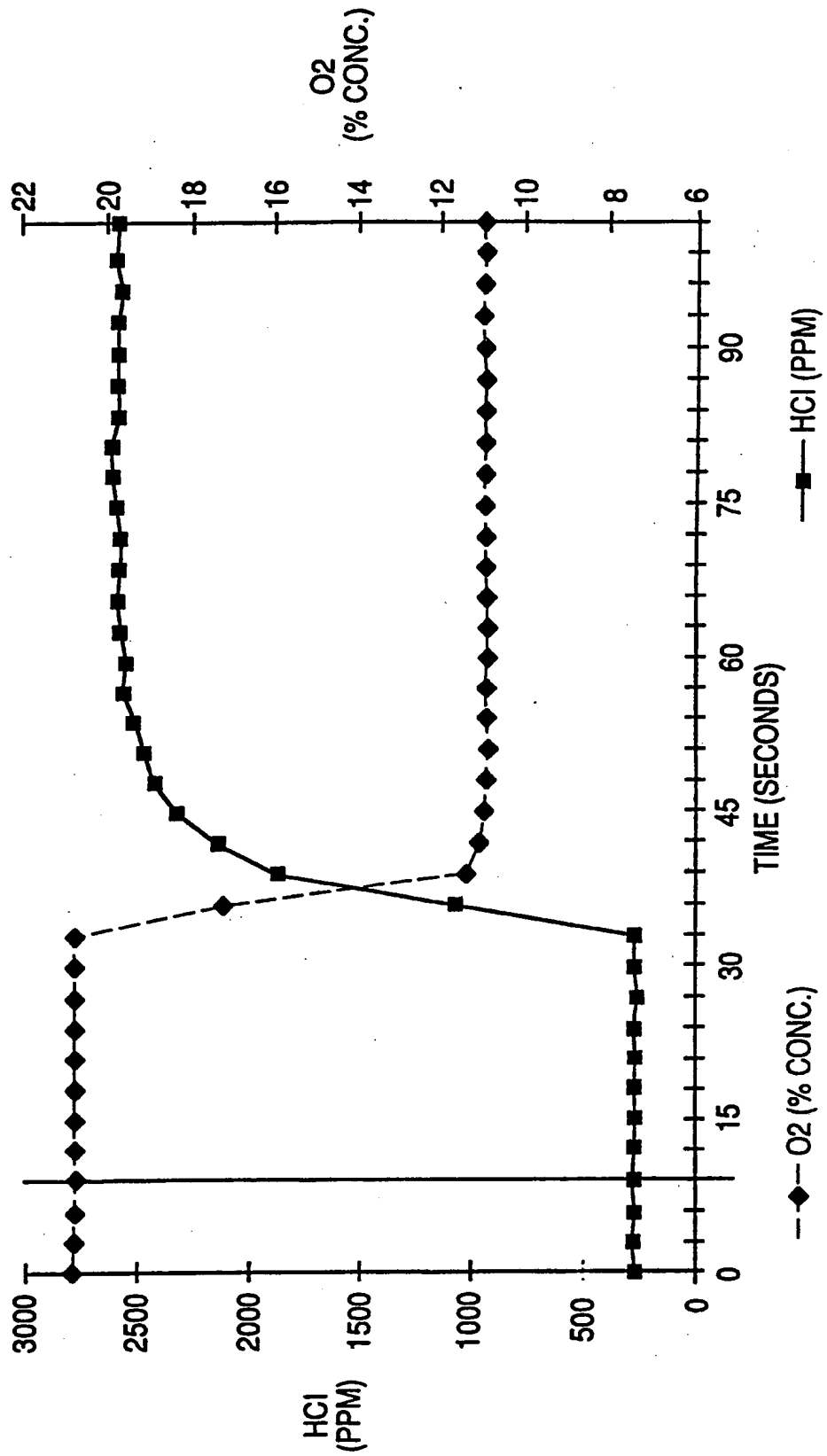


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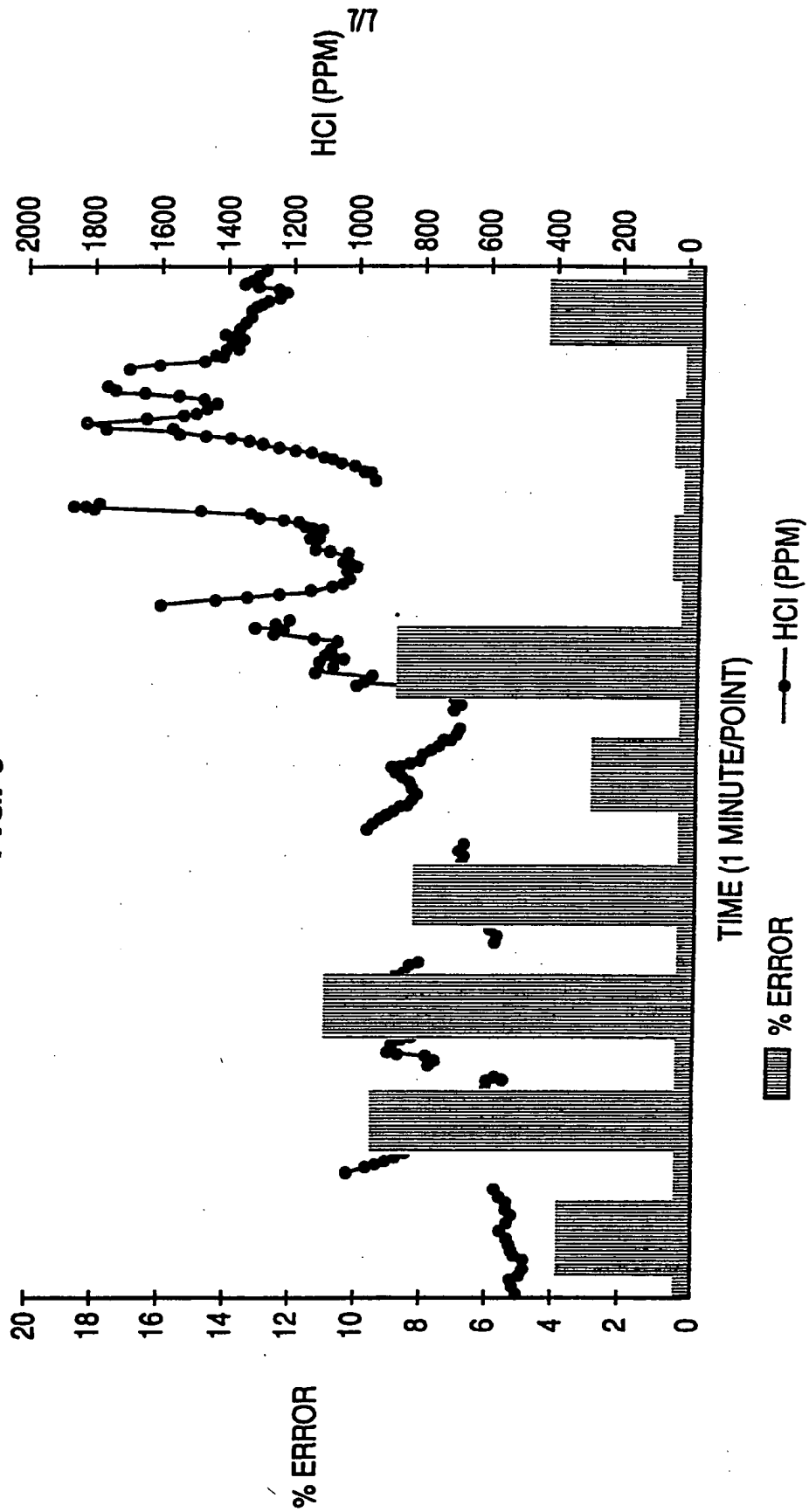
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FIG. 5b



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FIG. 6



INTERNATIONAL SEARCH REPORT

PCT/US 91/07449

International Application No

I. CLASSIFICATION F SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 G01N1/24; G01N33/00

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

G01N

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸**III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹**

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP,A,0 194 955 (INSTITUT DE RECHERCHE DE LA SIDERURGIE FRANCAISE) 17 September 1986 see column 1, line 1 - column 2, line 35	1,2,7
A	DE,U,8 421 369 (BERNATH, TIBOR) 6 August 1987 see page 1 - page 2	1,7
A	GB,A,1 496 887 (BRITISH PETROLEUM) 5 January 1978 see column 2, line 2 - line 9; figure	1,2,7
A	NASA TECH BRIEFS. vol. 1, no. 1, 1976, WASHINGTON US page 6: R A BARTERA ET AL: 'CONTINUOUS HCL IN AIR INDICATOR' see the whole document	1
	-/-	

¹⁰ Special categories of cited documents:^{"A"} document defining the general state of the art which is not considered to be of particular relevance^{"E"} earlier document but published on or after the international filing date^{"I"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)^{"O"} document referring to an oral disclosure, use, exhibition or other means^{"P"} document published prior to the international filing date but later than the priority date claimed^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention^{"X"} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step^{"Y"} document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.^{"A"} document member of the same patent family**IV. CERTIFICATION**

Date of the Actual Completion of the International Search

18 FEBRUARY 1992

Date of Mailing of this International Search Report

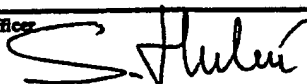
- 4. 03. 92

International Searching Authority

EUR PEAN PATENT FFICE

Signature of Authorized Officer

HULNE S.L.



III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	TECHNISCHES MESSEN TM. vol. 54, no. 5, 1987, MUNCHEN DE pages 195 - 199; M. ASCHERFELD: 'BEHEIZBARES GASANALYSENSYSTEM ZUR KONTINUIERLICHEN EXTRAKTIVEN MESSUNG.' see page 195 - page 196, right column; figures 2,3 ---	1,7
P,A	US,A,4 974 455 (G F MCGOWAN) 4 December 1990 see column 2 see column 5, line 44 - column 6, line 22; claim 1; figure 4 ---	1,2,7

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9107449
SA 52979**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 18/02/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0194955	17-09-86	FR-A- 2578325	05-09-86
DE-U-8421369	06-08-87	None	
GB-A-1496887	05-01-78	None	
US-A-4974455	04-12-90	None	